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80469 München (DE)(54) **EPOXY RESIN COMPOSITION, EPOXY RESIN COMPOSITION FOR FIBER-REINFORCED COMPOSITE, AND FIBER-REINFORCED COMPOSITE CONTAINING THE SAME**

(57) An object of the invention is to provide an epoxy resin composition having a low viscosity around a room temperature and excellent reinforcing fiber impregnating properties, thereby to provide a composite material having excellent heat resistance and mechanical properties including compressive strength.

composition after a lapse of  $t_c$  (min) at  $T_c$  (°C).

According to the present invention there is provided an epoxy resin composition comprising an aromatic epoxy resin having at least di-functionality, an aromatic amine compound and/or an alicyclic amine compound, wherein 5 minutes after the main agent comprising the epoxy resin and the curing agent comprising the aromatic amine compound and/or the alicyclic amine compound are mixed, the composition shows a viscosity at 25°C in the range of from 1 to 1500 mPas, and  $T_c$ ,  $t_c$ , and  $T_g$  satisfy the following equation.

$$T_g \geq T_c + 20 - k \times (T_c - 90) \quad (1)$$

 $k = 0$  when  $60 \leq T_c < 90$  $k = 0.35$  when  $90 \leq T_c \leq 200$  $T_c$ : highest temperature (°C) during the curing process ( $60 \leq T_c \leq 200$ ) $t_c$ : retention time (min) at the highest temperature ( $1 \leq t_c \leq 120$ ) $T_g$ : glass transition temperature of the epoxy resin

EP 1 094 087 A1

## Description

## Technical Field

[0001] The present invention relates to epoxy resin compositions. More particularly it relates to an epoxy resin composition for a fiber-reinforced composite material which has a low viscosity and can be easily handled for impregnating reinforcing fibers, and the resulting fiber-reinforced composite materials obtained after the composition is cured has excellent heat resistance and mechanical properties including good compressive strength, and to the fiber-reinforced composite materials obtained therefrom.

## Background Art

[0002] As fiber-reinforced composite materials comprising reinforcing fibers and matrix resins are lightweight and have excellent mechanical properties, they have been widely used in various fields including aerospace, sports and general industrial fields.

[0003] A thermosetting resin is predominantly employed for the matrix resin of the fiber-reinforced composite. Among them, an epoxy resin having excellent heat resistance, high elastic modulus and good chemical resistance, as well as a little shrinkage on curing is most commonly employed.

[0004] For producing fiber-reinforced composite materials, various methods, such as prepreg method, hand lay-up method, filament winding method, pull-trusion method, and RTM (resin transfer molding) method have been employed.

[0005] Among them, the RTM method, in which a preform comprising reinforcing fibers is placed in a mold, and a resin is poured thereinto to impregnate the preform and cured to produce a molded product, has a great advantage that a large member having a complicated shape can be molded in a short time.

[0006] The resin for use in RTM method needs to have a low viscosity to facilitate the impregnation of the preform. If the viscosity of the resin is high, a longer time is required for injection, which may result in a low productivity or provide unimpregnated portions of the obtained fiber-reinforced composite materials. In the RTM method, the viscosity of the resin can also be lowered by raising the temperature of the resin, however, in the case of molding a large member, the entire mold must be heated, therefore it is greatly disadvantageous from the view point of the facility and the required energy. Furthermore, the curing of the resin may be progressed by the heat during the injection process, which may result in an increase of the viscosity of the resin. Therefore, a resin requiring no heating and having a sufficiently low viscosity around the room temperature has been strongly desired.

[0007] As the thermosetting resin for use in the RTM method, epoxy resins are often employed. In addition to that, thermosetting resins for use in the RTM method include unsaturated polyester resins, vinyl ester resins, and phenol resins etc. Many of these unsaturated polyester resins, vinyl ester resins and phenol resins have low viscosities around the room temperature, therefore show good injection workability around the room temperature, however, epoxy resins are desirable to provide fiber-reinforced composite materials having excellent heat resistance and mechanical properties and to reduce the polymerization shrinkage during the curing reaction.

[0008] Unfortunately all the epoxy resins are either those having good heat resistance or mechanical properties of the resulting fiber-reinforced composite materials, but poor injection workability around the room temperature due to its high viscosity, or those having good injection workability due to its low viscosity at the room temperature but insufficient heat resistance or mechanical properties of the resulting fiber-reinforced composite materials, therefore when good heat resistance and mechanical properties are required for the molded product, the epoxy resins must be heated and employed in the RTM method. In the publication of Japanese Patent Laid-Open Hei 6-329763, an epoxy resin composition comprising an epoxy resin and diethyl toluene diamine as a curing agent has been disclosed, however there are problems that this composition still has a high viscosity and poor injection workability around the room temperature and the obtained fiber-reinforced composite materials have some parts which are not impregnated with the resin, therefore the desired mechanical properties are not attained.

## Disclosure of Invention

[0009] The epoxy resin compositions according to the present invention have the following construction in order to solve the above-mentioned problems. Accordingly an epoxy resin composition of the present invention comprises an aromatic epoxy resin having at least di-functionality, an aromatic amine compound and/or an alicyclic amine compound, and 5 minutes after the main agent comprising the epoxy resin and the curing agent comprising the aromatic amine compound and/or the alicyclic amine compound are mixed at 25°C, its viscosity at 25°C is within the range of from 1 to 1500 mPas, and  $T_g$ ,  $T_c$ , and  $T_g$  satisfy the following equation.

$$T_g \geq T_c + 20 - k \times (T_c - 90) \quad (1)$$

$k = 0$  when  $60 \leq T_c < 90$

$k = 0.35$  when  $90 \leq T_c \leq 200$

$T_c$ : highest temperature ( $^{\circ}\text{C}$ ) during the curing process ( $60 \leq T_c \leq 200$ )

$t_c$ : retention time (min) at the highest temperature ( $1 \leq t_c \leq 120$ )

$T_g$ : glass transition point of the epoxy resin composition after a lapse of  $t_c$  (min) at  $T_c$  ( $^{\circ}\text{C}$ ).

#### Best Mode for Carrying Out the Invention

**[0010]** The present inventors have found that an epoxy resin composition in which an aromatic epoxy resin having at least di-functionality, and an aromatic amine compound and/or an alicyclic amine compound are blended (hereinafter simply referred to as an epoxy resin composition) can provide a greatly improved resin injection workability around a room temperature, i.e. around  $25^{\circ}\text{C}$  in the present invention, and greatly improved impregnation of reinforcing fibers with the resin, and that the resulting fiber-reinforced composite materials have both high heat resistance and good mechanical properties, and completed the present invention.

**[0011]** The epoxy resin composition according to the present invention comprises an aromatic epoxy resin having at least di-functionality. Here, the term "functionality" as used in di-functionality means an epoxy group. Also in the present invention, the term "epoxy resin" is used to refer to the monomer or oligomer as well, which are not yet polymerized or cured. The term "epoxy resin composition" means a composition in which the elements which are required for the polymerization or curing reaction are mixed, and the term "cured epoxy resin" (or "cured resin", or "cured product" or "cured product of an epoxy resin composition") refers to a product obtained after the polymerization or curing reaction is carried out. The term "aromatic epoxy resin" means an epoxy resin having an aromatic ring in one molecule. The aromatic epoxy resin having at least di-functionality is blended in order to impart excellent heat resistance and mechanical properties to the fiber-reinforced composite materials (hereinafter simply abbreviated as composite materials) as it reacts with a curing agent to form a crosslinked structure.

**[0012]** It is important that the epoxy resin composition has a sufficiently low viscosity around the room temperature in order to improve the impregnation of the reinforcing fibers. But a too low viscosity becomes a cause of providing unimpregnated portions and voids in the obtained molded products. From the view point of good injection workability, impregnating properties, and improved mixing of the main agent and the curing agent, the viscosity of the main agent and that of the curing agent at  $25^{\circ}\text{C}$  shall be respectively within the range of from 1 to 3000 mPas, preferably from 1 to 2000 mPas, more preferably from 1 to 1000 mPas.

**[0013]** According to the present invention, when the viscosity of the main agent at  $25^{\circ}\text{C}$  is within the range of from 2000 to 3000 mPas, the viscosity of the curing agent at  $25^{\circ}\text{C}$  is preferably within the range of from 1 to 500 mPas. When the viscosity of the main agent at  $25^{\circ}\text{C}$  is within the range of from 1000 to 2000 mPas, the viscosity of the curing agent at  $25^{\circ}\text{C}$  is preferably within the range of from 1 to 1000 mPas. Furthermore, when the viscosity of the main agent at  $25^{\circ}\text{C}$  is within the range of from 1 to 1000 mPas, the viscosity of the curing agent at  $25^{\circ}\text{C}$  is preferably within the range of from 1 to 3000 mPas.

**[0014]** Various methods can be employed depending on the applications in order to cure the epoxy resin composition which is obtained after the main agent and the curing agent are mixed. In one exemplary process, the temperature is raised at a fixed rate, and held constant for the length of  $t_c$  (min) after it reached the highest temperature  $T_c$  ( $^{\circ}\text{C}$ ), then lowered. Or the so-called Step-cure method can be another exemplary process, in which the temperature is raised at a fixed rate, and held constant for a certain time, then it is raised again until it reach the highest temperature  $T_c$  ( $^{\circ}\text{C}$ ), and held constant at that temperature, then it is lowered.

**[0015]** In order to attain a composite material having good heat resistance, the highest temperature  $T_c$  shall be within the range of from  $60^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  during the curing process of the epoxy resin composition. In order to raise the productivity, the time  $t_c$  for holding the highest temperature constant shall be within the range of from 1 to 120 minutes.

**[0016]** The glass transition point  $T_g$  of the epoxy resin composition at the time point when the composition is held at  $T_c$  ( $^{\circ}\text{C}$ ) for the length of  $t_c$  (min) is measured according to the method described in EXAMPLES, after the resulting cured product of the epoxy resin composition is cooled from  $T_c$  ( $^{\circ}\text{C}$ ) to the room temperature.

**[0017]** The heat resistance of the composite material is affected by the glass transition point  $T_g$  of the cured product of the epoxy resin composition, which is the matrix resin, and the glass transition point  $T_g$  generally changes depending on the  $T_c$  ( $^{\circ}\text{C}$ ) which is the highest temperature during the curing process and the  $t_c$  (min) the time during which the highest temperature is held constant.

**[0018]** According to the present invention, when the highest temperature  $T_c$  is in the low temperature region of not less than  $60^{\circ}\text{C}$  and less than  $90^{\circ}\text{C}$ , the glass transition point  $T_g$  of the resin composition, which is the matrix resin, is required to be higher than the highest temperature  $T_c$  by  $20^{\circ}\text{C}$  or more. That is, there must be  $T_c$ ,  $t_c$ , and  $T_g$  satisfying the following equation (1).

$$T_g \geq T_c + 20 \quad (1)$$

[0019] When the highest temperature  $T_c$  is in a high temperature region of not less than 90°C and not more than 200°C, there must be  $T_c$ ,  $t_c$  and  $T_g$  satisfying the following equation (1').

$$T_g \geq T_c + 20 - 0.35 \times (T_c - 90) \quad (1')$$

[0020] According to the present invention, the highest temperature  $T_c$  (°C) and the retention time  $t_c$  (min) satisfying the above-mentioned equation (1) or equation (1') are employed as the production conditions and composite materials are produced while the highest temperature  $T_c$  (°C) is held constant for the length of time  $t_c$  (min).

[0021] As the elastic modulus of the cured resin obtained by curing the epoxy resin composition affects the mechanical properties, in particular the compressive strength, of the composite material, according to the present invention, the tensile modulus of elasticity  $E$  of the cured resin plate determined by the following method shall be within the range of from 3.2 to 5 Gpa, preferably from 3.4 to 4.8 Gpa. When it is below 3.2 Gpa, the compressive strength of the composite material may be insufficient, however, when it is over 5 Gpa, the tenacity of the composite material may be insufficient.

[0022] According to the present invention, it is preferable that the main agent and the curing agent which will be discussed later, are mixed prior to the use to provide an epoxy resin composition, then the composition is injected and molded product such as a composite material is produced.

[0023] The epoxy resin composition of the present invention, after the main agent and the curing agent are mixed and allowed to stand at 25°C for 5 minutes, is required to have a viscosity at 25°C (hereinafter represented by  $\eta_5$ ) within the range of from 1 to 1500 mPas, preferably within the range of from 1 to 1000 mPas, more preferably within the range of from 10 to 700 mPas.

[0024] Furthermore, the epoxy resin composition of the present invention preferably has such a viscosity at 25°C after the main agent and the curing agent are mixed and allowed to stand at 25°C for 60 minutes (in mPas, abbreviated as  $\eta_{60}$ ) that satisfies the following equation (2);

$$1 \leq \eta_{60} \leq 1500 \quad (2)$$

more preferably the viscosity of the epoxy resin composition, which is allowed to stand at 25°C for 120 minutes and measured at 25°C (abbreviated as  $\eta_{120}$ ), is within the range of from 1 to 1500 mPas, particularly preferably the viscosity of the epoxy resin composition which is allowed to stand at 25°C for 240 minutes is desirably within the range of from 1 to 1500 mPas.

[0025] Or, the viscosity of the epoxy resin composition, which is allowed to stand at 25°C for 240 minutes,  $\eta_{240}$ , is desirably within the range of from 1 to 1000 mPas, more preferably it is within the range of from 10 to 700 mPas.

[0026]  $\eta_{60}$  and  $\eta_5$  of the epoxy resin composition according to the present invention are preferably such that  $\eta_{60}$  divided by  $\eta_5$  ( $\eta_{60}/\eta_5$ ) satisfies the following equation (3);

$$1 \leq \eta_{60}/\eta_5 \leq 3 \quad (3)$$

more preferably  $\eta_{120}/\eta_5$  is within the range of from 1 to 3, particularly preferably,  $\eta_{240}/\eta_5$  is within the range of from 1 to 3. The epoxy resin compositions out of these limits, may have lowered resin injection workability and reinforcing fiber impregnation properties.

[0027] The aromatic epoxy resin having at least di-functionality for use in the present invention is an epoxy resin having an aromatic ring and two or more epoxy groups in one molecule. Examples of the aromatic epoxy resins having two epoxy groups include the following compounds.

[0028] Firstly bisphenol type epoxy resins including bisphenol A type epoxy resins obtained from bisphenol A, bisphenol F type epoxy resins obtained from bisphenol F, bisphenol S type epoxy resins obtained from bisphenol S, and tetrabromobisphenol A type epoxy resins obtained from tetrabromobisphenol A. Commercially available bisphenol A type epoxy resins include EPICOAT 825 (epoxy equivalent 172 - 178), EPICOAT 828 (epoxy equivalent 184 - 194), EPICOAT 834 (epoxy equivalent 230 - 270), EPICOAT 1001 (epoxy equivalent 450 - 500), EPICOAT 1002 (epoxy equivalent 600 - 700), EPICOAT 1003 (epoxy equivalent 670 - 770), EPICOAT 1004 (epoxy equivalent 872 - 975), EPICOAT 1007 (epoxy equivalent 1750 - 2200), EPICOAT 1009 (epoxy equivalent 2400 - 3300), EPICOAT 1010 (epoxy equivalent 3000 - 5000) (all of these are registered trademark, manufactured by Yuka Shell Epoxy K.K.), EPOTOTO YD-128 (epoxy equivalent 184 - 194), EPOTOTO YD-011 (epoxy equivalent 450 - 500), EPOTOTO YD-014 (epoxy equivalent 900 - 1000), EPOTOTO YD-017 (epoxy equivalent 1750 - 2100), EPOTOTO YD-019 (epoxy equivalent 2400 - 3000), EPOTOTO YD-022 (epoxy equivalent 4000 - 6000) (all of these are registered trademark, manufactured by Toto Kasei K.K.), EPICRON 840 (epoxy equivalent 180 - 190), EPICRON 850 (epoxy equivalent 184 - 194), EPICRON 1050 (epoxy equivalent 450 - 500), EPICRON 3050 (epoxy equivalent 740 - 860), EPICRON HM-101 (epoxy equivalent 3200 - 3900) (all of these are registered trademark, manufactured by Dainippon Ink & Chemicals Inc.), SUMIEPOXY ELA-128

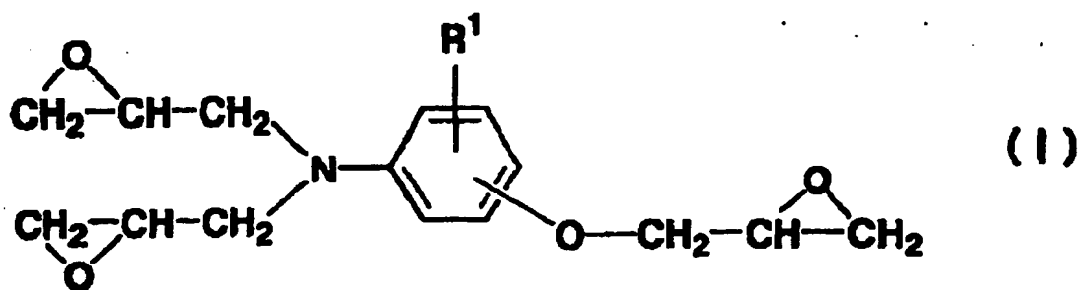
(registered trademark, epoxy equivalent 184 - 194, manufactured by Sumitomo Chemical Co., Ltd.), DER 331 (registered trademark, epoxy equivalent 182 - 192, manufactured by The Dow Chemical Co.) and the like. Commercially available bisphenol F type epoxy resins include EPICOAT 806 (epoxy equivalent 160 - 170), EPICOAT 807 (epoxy equivalent 160 - 175), EPICOAT E4002P (epoxy equivalent 610), EPICOAT E4003P (epoxy equivalent 800), EPICOAT E4004P (epoxy equivalent 930), EPICOAT E4007P (epoxy equivalent 2060), EPICOAT E4009P (epoxy equivalent 3030), EPICOAT E4010P (epoxy equivalent 4400) (all of these are registered trademark, manufactured by Yuka Shell Epoxy K.K.), EPICRON 830 (registered trademark, epoxy equivalent 170 - 190, manufactured by Dainippon Ink & Chemicals Inc.), EPOTOTO YDF-2001 (epoxy equivalent 450 - 500), EPOTOTO YDF-2004 (epoxy equivalent 900 - 1000) (all of these are registered trademark, manufactured by Toto Kasei K.K.) and the like. Commercially available bisphenol S type epoxy resins include DENACOL EX-251 (registered trademark, manufactured by Nagase Chemicals Ltd., epoxy equivalent 189). Commercially available tetrabromobisphenol A type epoxy resin include EPICOAT 5050 (registered trademark, manufactured by Yuka Shell Epoxy K.K., epoxy equivalent 380 - 410), EPICRON 152 (manufactured by Dainippon Ink & Chemicals Inc., epoxy equivalent 340 - 380), SUMIEPOXY ESB-400T (manufactured by Sumitomo Chemical Co., Ltd., epoxy equivalent 380 - 420), EPOTOTO YBD-360 (manufactured by Toto Kasei K.K., epoxy equivalent 350 - 370).

[0029] In addition to those, DENACOL EX-201, resorcin glycidyl ether (registered trademark, manufactured by Nagase Chemicals Ltd., epoxy equivalent 118), DENACOL EX-203, hydroquinone diglycidyl ether (registered trademark, manufactured by Nagase Chemicals Ltd., epoxy equivalent 112), EPICRON HP-4032H, diglycidyl ether of 1,6-dihydroxynaphthalene (registered trademark, manufactured by Dainippon Ink & Chemicals Inc., epoxy equivalent 250), EPON HPT RESIN 1079, diglycidyl ether of 9,9-bis(4-hydroxyphenyl)fluorene (registered trademark, manufactured by Shell Chemical Co., epoxy equivalent 250 - 260) can be employed as well.

[0030] Further examples include GAN, diglycidyl aniline (registered trademark, manufactured by Nippon Kayaku Co., Ltd., epoxy equivalent 115 - 135) and glycidyl esters such as diglycidyl phthalate, diglycidyl terephthalate and the like.

[0031] According to the present invention, one method of imparting better heat resistance and mechanical properties to the composite materials is contemplated to increase the crosslinking density of the matrix resin. For such a purpose, it is preferable to blend an aromatic epoxy resin having at least tri-functionality. The amount of the aromatic epoxy resin having at least tri-functionality in the total amount of epoxy resins is preferably 50 - 100 % by weight (more preferably 60 - 100 % by weight, further preferably 70 - 100 % by weight).

[0032] According to the present invention, an aromatic epoxy resin having tri-functionality represented by the chemical formula (I) is preferably blended.

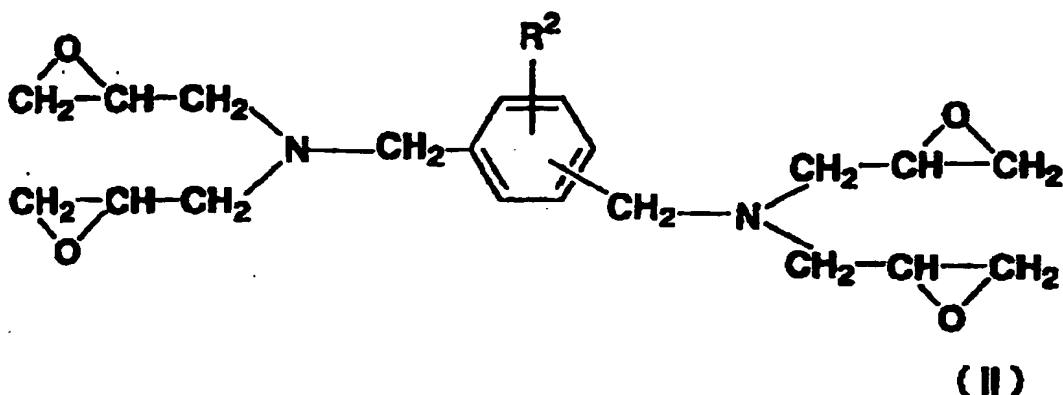


(wherein R<sub>1</sub> is hydrogen atom or an alkyl group having approximately 1 - 4 carbon atoms).

[0033] Commercially available examples of such epoxy resin include EPICOAT 630 (registered trademark, manufactured by Yuka Shell Epoxy K.K., N,N-diglycidyl-p-glycidyl oxyaniline, viscosity in 25°C environment: 600 - 700 mPas), ARALDITE MY0510 (registered trademark, manufactured by CIBA, N,N-diglycidyl-p-glycidyl oxyaniline, viscosity in 25°C environment: 550 - 850 mPas), SUMIEPOXY ELM100 (registered trademark, manufactured by Sumitomo Chemical Co., Ltd., N,N-diglycidyl-4-glycidyl-2-methylaniline, viscosity in 50°C environment: 1000 - 1700 mPas), SUMIEPOXY ELM120 (registered trademark, manufactured by Sumitomo Chemical Co., Ltd., N,N-diglycidyl-m-glycidyl oxyaniline, viscosity in 50°C environment: 1500 - 3000 mPas) and the like. Among them, EPICOAT 630 and ARALDITE MY0510 are particularly preferable due to their low viscosities.

[0034] The epoxy resin represented by chemical formula (I) can be blended alone or in admixture of two or more kinds.

[0035] According to the present invention, an aromatic epoxy resin having tetra-functionality such as those represented by chemical formula (II) can also be blended.



(wherein  $R_2$  is hydrogen atom or an alkyl group having approximately 1 - 4 carbon atoms.)

**[0036]** Commercially available examples of such epoxy resin include TETRAD-X (registered trademark, manufactured by Mitsubishi Gas Chemical Co., Inc., N,N,N',N'-tetraglycidyl-m-xylylene diamine, viscosity in 25°C environment: 1600 - 2500 mPas) and the like. The epoxy resin represented by chemical formula (II) can be blended alone or in admixture with an epoxy resin represented by chemical formula (I).

**[0037]** An aromatic epoxy resin having at least tri-functionality has a viscosity at 25°C preferably within the range of from 1 to 3000 mPas, more preferably within the range of from 1 to 2000 mPas, particularly preferably within the range of from 1 to 1000 mPas. The viscosity of the aromatic epoxy resin being over 3000 mPas results in a high viscosity of the epoxy resin composition and the reinforcing fiber impregnation properties may be lowered.

**[0038]** The upper limit to the functionality of the aromatic epoxy resin is not particularly limited, however, if the crosslinking density of the matrix resin in the composite material becomes too high, it may bring brittleness and result in insufficient tenacity of the composite material disadvantageously. Taking those into consideration, the weight average number of functionality of the aromatic epoxy resin is preferably 2 - 6 (more preferably 2 - 5, further preferably 2 - 4).

**[0039]** Another method which can be envisaged to obtain excellent heat resistance and mechanical properties of the composite material according to the present invention is to link crosslinking points in the matrix resin with a rigid skeleton. However, when an epoxy resin comprising a rigid skeleton is blended, as the molecules have small degrees of internal freedom, the viscosity of the epoxy resin composition may be increased in some cases. In order to solve such a problem, an epoxy resin having a low molecular weight (preferably between 100 and 500) can be employed. Examples of an epoxy resin having a rigid skeleton and a low molecular weight include biphenyl type epoxy resins.

**[0040]** Commercially available examples of such an epoxy resin include EPICOAT YX4000 (registered trademark, manufactured by Yuka Shell Epoxy K.K., 4,4'-dihydroxy-3,3',5,5'-tetramethylbiphenyl diglycidyl ether), EPICOAT YX4000H (registered trademark, manufactured by Yuka Shell Epoxy K.K., 4,4'-dihydroxy-3,3',5,5'-tetramethylbiphenyl diglycidyl ether), EPICOAT YL6121L (registered trademark, manufactured by Yuka Shell Epoxy K.K., 4,4'-dihydroxy-3,3',5,5'-tetramethylbiphenyl diglycidyl ether) and the like.

**[0041]** In order to optimize the viscosity of the epoxy resin composition according to the present invention, an epoxy resin having a low viscosity can be blended in addition to the aromatic epoxy resin having at least di-functionality.

**[0042]** Examples of such an epoxy resin having a low viscosity include glycidyl ether type aliphatic epoxy resins having at least di-functionality.

**[0043]** In order to raise the heat resistance and improve mechanical properties including compressive strength and the like, of the composite material according to the present invention, it is preferable that the glycidyl ether type aliphatic epoxy resin having at least di-functionality satisfies the following equation (4), more preferably equation (4').

$$0 \leq \alpha \leq 4 \quad (4)$$

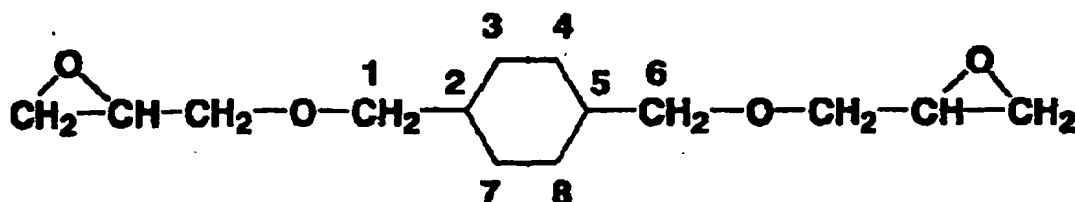
$$0 \leq \alpha \leq 3 \quad (4')$$

**[0044]** Here,  $\alpha$  shows a number of (carbon) atoms which do not belong to a ring in the molecular chain which is produced by linking any two glycidyl oxy groups in a glycidyl ether type aliphatic epoxy resin having at least di-functionality, provided that the molecular chain has the largest number of (carbon) atoms which do not belong to a ring.

**[0045]**  $\alpha$  is an index showing flexibility of the molecular chain. The bigger the  $\alpha$  is, the more flexible the molecular

chain is, thereby the network structure of the matrix resin in the composite material becomes more flexible, and the heat resistance and the mechanical properties of the composite material tend to become insufficient. The method in which a is obtained from the molecular structure of the epoxy resin will be explained in detail as follows.

[0046] The glycidyl ether type aliphatic epoxy resin having at least di-functionality, represented by the following chemical structure is taken as an example and the  $\alpha$  thereof is obtained.

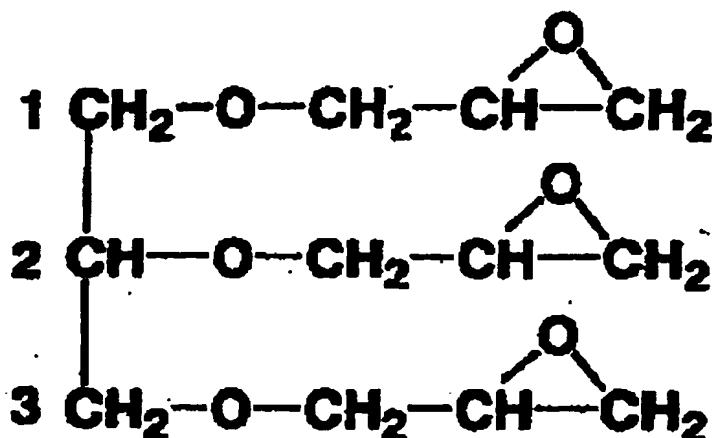


[0047] There can be two molecular chains linking two glycidyl groups as follows.

1-2-3-4-5-6  
1-2-7-8-5-6

[0048] The number of the (carbon) atoms which do not belong to a ring are two in both cases. Accordingly,  $\alpha$  is 2.

[0049] Then a glycidyl ether type aliphatic epoxy resin having at least di-functionality represented by the following chemical structure is taken as an example and the  $\alpha$  thereof is obtained.

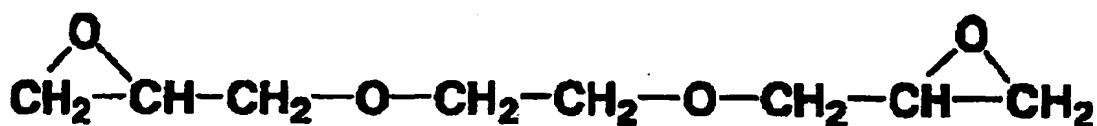


[0050] There can be three molecular chains linking three glycidyl groups as follows.

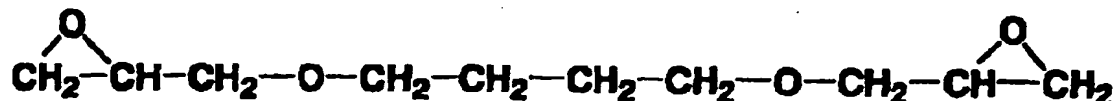
1 - 2  
2 - 3  
1 - 2 - 3

[0051] In the first and the second cases, the number of the (carbon) atoms which do not belong to a ring is 2, and in the third case, the number of the atoms which do not belong to a ring is 3. Therefore,  $\alpha$  is 3.

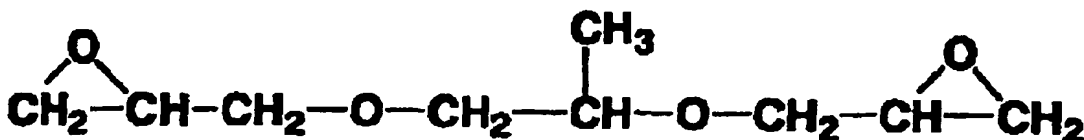
[0052] Commercially available examples of such a glycidyl ether type aliphatic epoxy resin having at least di-functionality, include the following products. DENACOL EX 810 (registered trademark, manufactured by Nagase Kasei Kogyo K.K., viscosity in 25°C environment: 15 mPas,  $\alpha=2$ , represented by the following chemical formula)



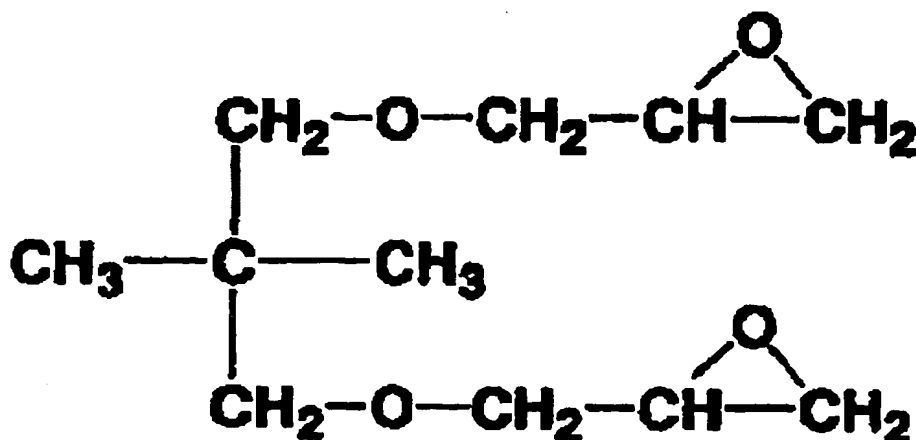
HELOXY 67 (registered trademark, manufactured by Yuka Shell Epoxy K.K., viscosity in 25°C environment: 13 - 18 mPas,  $\alpha = 4$ , represented by the following chemical formula)



DENACOL EX911 (registered trademark, manufactured by Nagase Kasei Kogyo K.K., viscosity in 25°C: 20 mPas,  $\alpha = 2$ , represented by the following chemical formula)

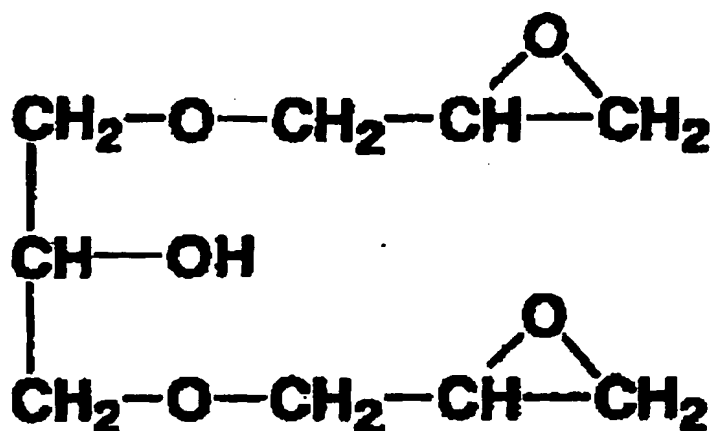


HELOXY 68 (registered trademark, manufactured by Yuka Shell Epoxy K.K., viscosity in 25°C environment: 13 - 18 mPas,  $\alpha = 3$ , represented by the following chemical formula)

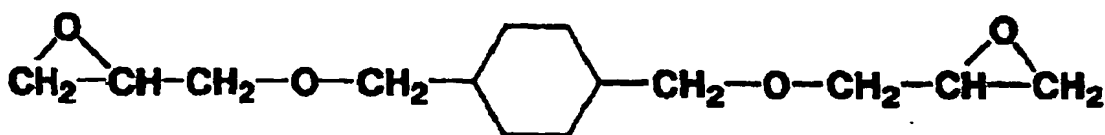


EPOLIGHT 80MF (registered trademark, manufactured by Kyoeisha Chemical Co., Ltd., viscosity in 25°C environment: 120 - 180 mPas,  $\alpha = 3$ , represented by the following chemical formula)

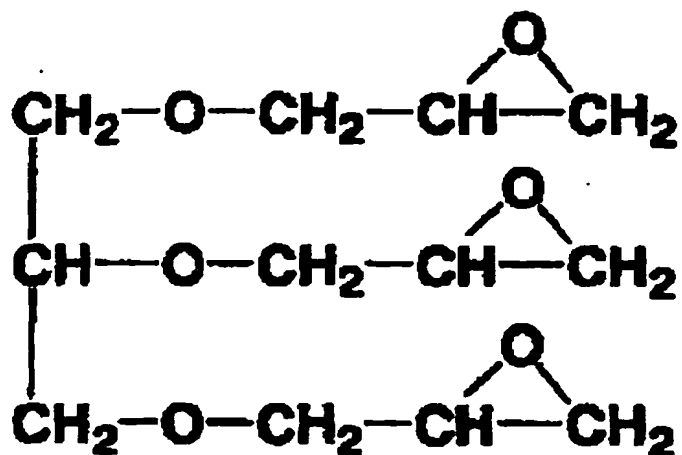




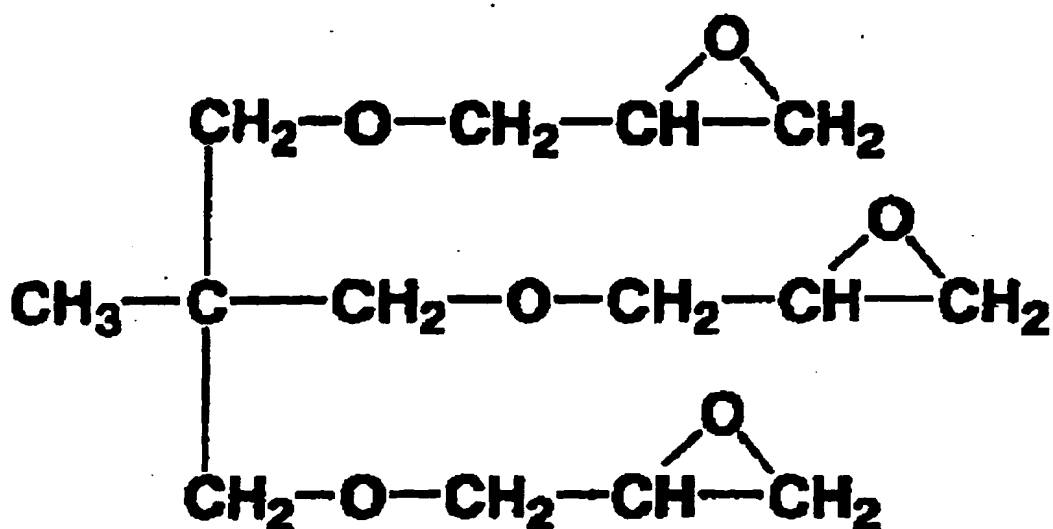
HELOXY 107 (registered trademark, manufactured by Yuka Shell Epoxy K.K., viscosity in 25°C environment: 55 - 75 mPas,  $\alpha = 2$ , represented by the following chemical formula)



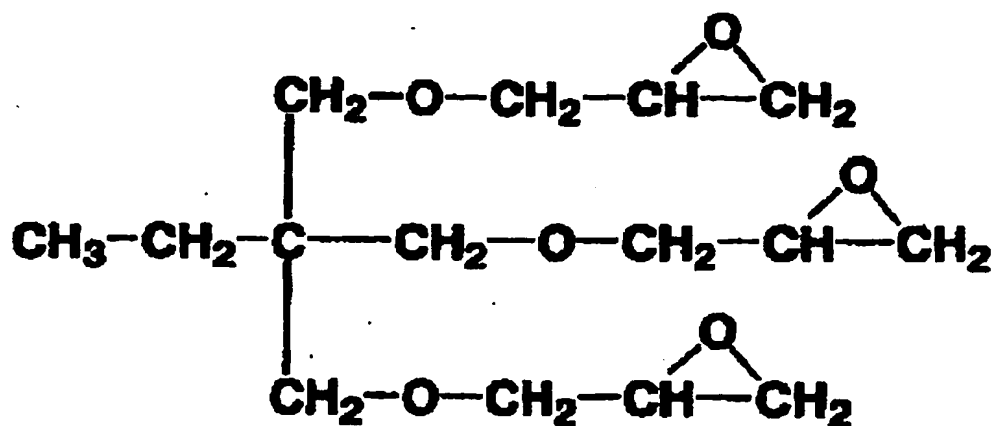
DENACOL EX313 (registered trademark, manufactured by Nagase Kasei Kogyo K.K., viscosity in 25°C: 150 mPas,  $\alpha = 3$ , represented by the following chemical formula)



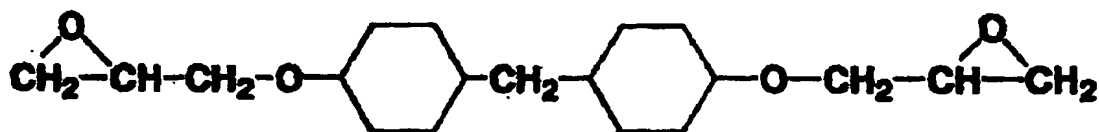
HELOXY 44 (registered trademark, manufactured by Yuka Shell Epoxy K.K., viscosity in 25°C environment: 200 - 330 mPas,  $\alpha = 3$ , represented by the following chemical formula)



HELOXY 48 (registered trademark, manufactured by Yuka Shell Epoxy K.K., viscosity in 25°C environment: 125 - 250 mPas,  $\alpha = 3$ , represented by the following chemical formula)



YL 6753 (Model, manufactured by Yuka Shell Epoxy K.K., viscosity in 25°C environment: 400 mPas,  $\alpha = 1$ , represented by the following chemical formula)



[0053] These glycidyl ether type aliphatic epoxy resins having at least di-functionality can be blended alone or blended in admixture of two or more kinds.

[0054] The amount of the blended glycidyl ether type aliphatic epoxy resins having at least di-functionality (the total amount when two or more kinds are employed) is preferably 1 - 50 % by weight (more preferably 1 - 30 % by weight, further preferably 1 - 10 % by weight) based on the total amount of the epoxy resin as 100 % by weight. When it exceeds

50 % by weight, the heat resistance and mechanical properties, such as compressive strength, of the composite material may become insufficient.

[0055] Glycidyl ether type aliphatic epoxy resins having at least di-functionality have generally lower viscosities compared to the above-mentioned aromatic epoxy resins. A glycidyl ether type aliphatic epoxy resin having at least di-functionality preferably has a viscosity in 25°C environment within a range of from 1 to 500 mPas, preferably 1 - 300 mPas, more preferably 1 - 100 mPas. When it exceeds 500 mPas, the viscosity of the epoxy resin composition becomes too high and the reinforcing fiber impregnation properties may be lowered.

[0056] The upper limit to the number of functionality of the glycidyl ether type aliphatic epoxy resins having at least di-functionality is not particularly limited, however, if the crosslinking density of the matrix resin in the composite material becomes too high, it may bring brittleness and result in insufficient tenacity of the composite material disadvantageously. Taking those into consideration, the weight average number of functionality of the glycidyl ether type aliphatic epoxy resins is preferably 2 - 6 (more preferably 2 - 5, further preferably 2 - 4).

[0057] The epoxy resin composition according to the present invention comprises an aromatic amine compound and/or an alicyclic amine compound. These amine compounds are curing agents, mixed and reacted with the above-mentioned epoxy resins to provide a cured product.

[0058] The aromatic amine compound is a primary, secondary or tertiary amine having an aromatic ring, preferably a primary diamine having 6 - 25 (more preferably 6 - 17) carbon atoms. The alicyclic amine compound is a primary, secondary or tertiary amine having an alicyclic ring, and preferably a primary diamine having 6 - 25 (more preferably 6 - 15) carbon atoms.

[0059] When the aromatic amine compound is blended, the aromatic amine compound preferably has a viscosity in 25°C environment of within the range of from 1 to 3000 mPas, more preferably within the range of from 1 to 2000 mPas, particularly preferably within the range of from 1 to 1000 mPas. When it exceeds 3000 mPas, the viscosity of the epoxy resin composition becomes too high and the impregnation of the reinforcing fibers may be lowered.

[0060] Commercially available examples of the aromatic amine compound include EPICURE W (registered trademark, manufactured by Yuka Schell Epoxy K.K, a mixture of 2,4-diethyl-6-methyl-m-phenylene diamine and 4,6-diethyl-2-methyl-m-phenylene diamine, viscosity in 25°C environment: 100 - 400 mPas), KAYAHARD A-A (registered trademark, manufactured by Nippon Kayaku Co., Ltd., 2,2'-diethyl-4,4'-methylene dianiline, viscosity in 25°C environment: 2000 - 3000 mPas), KAYAHARD A-B (registered trademark, manufactured by Nippon Kayaku Co., Ltd., a mixture of 2,2'-diethyl-4,4'-methylene dianiline and 4,4'-methylene dianiline, viscosity in 25°C environment: 1500 - 2500 mPas).

[0061] When an alicyclic amine compound is blended, the alicyclic amine compound preferably has a viscosity in 25°C environment within the range of from 1 to 500 mPas, preferably within the range of from 1 to 300 mPas. When it exceeds 500 mPas, the viscosity of the epoxy resin composition becomes too high and the impregnation of the reinforcing fibers may be lowered. In order to raise the heat resistance and mechanical properties including compressive strength and the like of the composite material, it is preferable that the alicyclic amine compound satisfies the following equation (5), more preferably equation (5').

$$0 \leq \beta \leq 4 \quad (5)$$

$$0 \leq \beta \leq 3 \quad (5')$$

[0062] Here,  $\beta$  shows a number of (carbon) atoms which do not belong to a ring in the molecular chain which is produced by linking any two amino groups in an alicyclic amine compound, provided that the molecular chain has the largest number of (carbon) atoms which do not belong to a ring.

[0063]  $\beta$  is an index showing flexibility of the molecular chain. The bigger the  $\beta$  is, the more flexible the molecular chain is, thereby the network structure of the matrix resin in the composite material becomes more flexible, and the heat resistance and the mechanical properties of the composite material tend to become insufficient.

[0064] If two or more kinds of alicyclic amine compounds having different  $\beta$  values exist, the overall  $\beta$  value shall be calculated by molal average.

[0065] An alicyclic amine compound preferably has an amino group in the molecule bonded to the secondary or tertiary carbon to prevent the viscosity of the epoxy resin composition from rising too much. This is because the amine bonded to the primary carbon generally reacts with an epoxy group at a higher reaction rate than the amine bonded to the secondary carbon or the tertiary carbon. In order to fully express such effects, the number of amino groups bonded to the secondary or tertiary carbon atoms is desirably in an amount of 50% or more, more preferably 70% or more, further preferably 90% or more of all the amino groups in the entire alicyclic amine compounds.

[0066] In addition to that, all the amino groups in the alicyclic amine compound are preferably bonded to such carbon atoms that constitute the ring structure, in order to improve the heat resistance and mechanical properties such as compressive strength of the composite material.

[0067] Commercially available alicyclic amine compounds include AMICURE PACM (registered trademark, manu-

factured by Air Products, 4,4'-methylene bis cyclohexyl amine, viscosity in 25°C environment: 80 mPas,  $\beta=1$ ), ANCAMINE 2090 (registered trademark, manufactured by Air Products, 2,2'-dimethyl-4,4'-methylene bis cyclohexyl amine, viscosity in 25°C environment: 120 mPas,  $\beta=1$ ), DCH-99 (Type, manufactured by E.I. du Pont de Nemours and Company, 1,2-cyclohexane diamine, viscosity in 21°C environment: 7 mPas,  $\beta=0$ ), 1,8-menthene diamine (manufactured by Sigma-Aldrich Co., viscosity in 25°C environment: 80 mPas,  $\beta=1$ ), isophorone diamine (manufactured by Hyurs Co., viscosity in 25°C environment: 13 mPas,  $\beta=1$ ), 1,3-bis aminomethyl cyclohexane (produced by Mitsubishi Gas Chemical Co., Inc, viscosity in 25°C environment: 9 mPas,  $\beta=2$ ), 2,5(6)-bis amino methyl norbornane (produced by Mitsui Chemicals Inc., viscosity in 25°C environment: 16 mPas,  $\beta=2$ ) and the like.

[0068] According to the present invention, an amine compound except for an aromatic amine compound and an alicyclic amine compound can be blended as a curing agent as well.

[0069] According to the present invention, the number of the active hydrogen (active hydrogen is a hydrogen atom which is bonded to nitrogen, oxygen and sulfur etc in an organic compound and has high reactivity, and plays a big role in crosslinking reaction) of the amine compound contained in the epoxy resin composition is preferably within the range of from 4 to 24, more preferably from 4 to 16, further preferably from 4 to 8. When it is below the lower limit of the above-mentioned numerical range, the crosslinking density of the matrix resin is reduced and heat resistance and elastic modulus are lowered, therefore the heat resistance and mechanical properties including compressive strength of the composite material tend to be lowered. When it exceeds the upper limit, the crosslinking density of the matrix resin in the composite material is increased too much and that brings brittleness, and the tenacity of the composite material tends to become insufficient. When two or more kinds of amine compounds are mixed, the number of the active hydrogen shall be calculated by weight average. The amine compound having 4 or more active hydrogen atoms is preferably present in an amount of 50 - 100%, based on the total amine compounds.

[0070] Though it depends on the cases, the ratio of the aromatic amine compound and/or the alicyclic amine compound based on the total amine compounds is preferably 50 - 100% by weight.

[0071] The main agent and the curing agent are preferably mixed at a mixing ratio which is decided according to the following equation (6);

$$0.5 \leq R/Re \leq 2 \quad (6)$$

wherein, R is the ratio of the curing agent to the main agent by weight, Re is the ratio of the epoxy groups (in mole) per 1 g of the main agent to the active hydrogen atoms (in mole) per 1 g of the curing agent.

[0072] According to the present invention, appropriate curing promoters can be blended as well for the purpose of reducing the highest temperature Tc (°C) and retention time tc (min). As the curing promoter, any known promoter can be used. More specifically, sulfonic esters disclosed in the specification of USP No.5,688,877, and sulfonium salts disclosed in the specification of USP No.4,554,342 can be preferably employed. According to the present invention, coloring agents, surfactants, and fire retardant additives can be blended as well according to each purpose. Provided that the ratio of the epoxy resin (including the curing agent) to the resin matrix (excluding the reinforcing fibers, or fillers in the form of a granule and a short fiber and the like) is preferably not less than 80 % by weight.

[0073] The epoxy resin composition according to the present invention is preferably employed for producing a composite material by the use of RTM method. In an Overview regarding the general technology of the recent RTM method (SAMPE Journal, Vol.34, No.6, pp.7-19), the following molding methods similar to the RTM methods are introduced, i.e. VARTM (Vacuum-Assisted RTM), VIMP (Variable Infusion Molding Process), TERTM (Thermal-Expansion RTM), RARTM (Rubber-Assisted RTM), RIRM (Resin Injection Recirculation Molding), CRTM (Continuous RTM), CIRTM (Co-Injection Resin Transfer Molding), RLI (Resin Liquid Infusion), and SCRIMP (Seeman's Composite Resin Infusion Molding Process) etc. The epoxy resin Compositions according to the present invention can also be preferably employed in such a molding method that is similar to the RTM method.

[0074] Preforms for use in the RTM method are produced by processing reinforcing fibres such as carbon fiber, glass fiber, and aramid fiber and the like in the form of a mat, woven fabric, knitted fabric, braid, and unidirectional sheet and the like. In particular, carbon fibers are preferably employed in order to obtain a lightweight and strong member. The fiber content of the reinforcing fiber is preferably 30 - 85 % by weight.

[0075] The epoxy resin composition according to the present invention can be suitably employed for a method in which reinforcing fibers are impregnated with a liquid epoxy resin around a room temperature, illustratively hand lay-up method, filament winding method, and pull-trusion method and the like.

## EXAMPLES

[0076] The present invention will be described in detail by way of example. Various samples used for Examples and Comparative Examples were prepared and the physical properties thereof were determined under the following conditions. The results of these Examples and the Comparative Example are summarized in the Tables 1 - 5.

## A. Viscosity

[0077] Viscosity of the main agent and that of the curing agent were determined in 25°C environment, according to the viscosity measurement method of JIS Z8803 in which a cone and plate rotational viscometer is employed.

[0078] 100 g of an epoxy resin composition obtained by mixing the main agent and the curing agent (after the homogeneous dispersion was confirmed by visual observation, the dispersion was further stirred by spatula, for the total of about 3 minutes), was put into a polyethylene cup having a circular bottom of 25-mm radius, and a cylindrical portion having an inner diameter of 50 mm and a height of 75 mm, and the viscosity  $\eta_5$  at the time point after a lapse of 5 minutes at 25°C, the viscosity  $\eta_{60}$  at the time point after a lapse of 60 minutes at 25°C, the viscosity  $\eta_{120}$  at the time point after a lapse of 120 minutes at 25°C, and the viscosity  $\eta_{240}$  at the time point after a lapse of 240 minutes at 25°C were measured according to the above-mentioned method.

[0079] When the viscosity was from 1 to 100 mPas, E type viscometer (ELD type) manufactured by Tokisangyo was employed, and when the viscosity was from 100 to 50,000 mPas, E type viscometer (EHD type) manufactured by Tokisangyo was employed. The rotor of the E type viscometer had an angle of 1°34' and a diameter of 24 mm.

## B. Preparation of a cured resin plate

[0080] An epoxy resin composition obtained by mixing an epoxy resin and a curing agent was injected into a mold having a planar cavity with a thickness of 2 mm, and cured in an oven under the following curing conditions to give a cured resin plate having a thickness of 2 mm.

C. Glass transition point T<sub>g</sub>

[0081] Then a cured resin plate obtained according to the above-mentioned method B was tested by DMA method in accordance with SACMA SRM18R-94 for the glass transition point T<sub>g</sub>. Here, Dynamic Analyzer RDA-II type manufactured by Rheometrics was used and the measurement was carried out at the temperature rising speed of 5°C/min, measuring frequency of 1 Hz.

## D. Tensile modulus of elasticity

[0082] From the cured resin plate obtained according to the above-mentioned method B, was prepared a small No.1 (No.1/2) test specimen and it was subjected to measurement according to JIS K7113 by using TENSILON in 23°C environment to give a stress-strain curve. The tensile modulus of elasticity E was obtained according to the following equation from the tensile stress  $\sigma_{0.001}$  (GPa) at the strain of 0.001, and the tensile stress  $\sigma_{0.003}$  (Gpa) at the strain of 0.003.

$$E(\text{Gpa}) = (\sigma_{0.003} - \sigma_{0.001}) / (0.003 - 0.001)$$

## E. Preparation of a composite material

[0083] A composite material was prepared by RTM method. A mold having a top force and a bottom force, having a cavity with a length of 200 mm, a width of 200 mm, and a height of 2.0 mm was employed. As a preform, 10 sheets of a carbon fiber woven fabric (Model:C07373, 193 g/m<sup>2</sup> manufactured by Toray Co.,) having a length of 190 mm and a width of 190 mm were laminated such that the fibers were aligned in the same direction.

[0084] Firstly, the preform was set in the cavity of the mold and a vacuum pump was connected to a suction inlet (at one point) provided on the side surface of the mold, and the pressure inside of the mold was reduced to not more than 0.1 mmHg, then a resin composition obtained by mixing the main agent and the curing agent, followed by being allowed to stand under a reduced pressure for 30 minutes to carry out de-gassing, was poured through the resin inlet provided at the center of the top force and the preform was impregnated therewith. At the time point when the resin was flowed out from the suction inlet, the resin inlet then the suction inlet were closed and the mold was heated in an oven to cure the resin composition to give a planar composite material.

## F. 0° Compressive strength

[0085] The planar composite material obtained in the above-mentioned method E was subjected to measurement for 0° compressive strength according to method A of JIS K7076.

# EXAMPLE 1

[0086] EPICOAT 630 was employed as an epoxy resin, and EPICURE W was employed as a curing agent and the viscosity of each material and the viscosity  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio (the ratio of the weight of the main agent to the weight of the curing agent, hereinafter referred to as mixing ratio R) was set to 0.464.

[0087] Then a cured resin plate was prepared according to the following procedure;

- (1) raising the temperature of the composition at 1.5°C/min to 180°C,
- (2) maintaining the temperature at 180° C for 120 minutes, and
- (3) lowering the temperature at 2.5°C/min to 25°C.

[0088] The obtained cured resin plate was subjected to the measurement for the glass transition point Tg and the tensile modulus of elasticity E.

# EXAMPLE 2

[0089] EPICOAT 630 was employed as an epoxy resin, and ANCAMINE 2049 was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio R was set to 0.613.

[0090] Then a cured resin plate was prepared according to the following procedure;

- (1) raising the temperature of the composition at 1.5°C/min to 60°C,
- (2) maintaining the temperature at 60°C for 180 minutes,
- (3) raising the temperature at 1.5°C/min to 180°C,
- (4) maintaining the temperature at 180°C for 120 minutes, and
- (5) lowering the temperature at 2.5°C/min to 25°C.

[0091] The obtained cured resin plate was subjected to the measurement for the glass transition point Tg and the tensile modulus of elasticity E.

# EXAMPLE 3

[0092] A mixture of 60 parts by weight of EPICOAT 630 and 40 parts by weight of EPICOAT 807 was employed as epoxy resins, and EPICURE W was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio R was set to 0.384.

[0093] Then a cured resin plate was prepared according to the procedure similar to that used in Example 1. The obtained cured resin plate was subjected to the measurement for the glass transition point Tg and the tensile modulus of elasticity E.

# EXAMPLE 4

[0094] A mixture of 70 parts by weight of EPICOAT 630 and 30 parts by weight of HELOXY 107 was employed as epoxy resins, and EPICURE W was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio R was set to 0.409.

[0095] Then a cured resin plate was prepared according to the procedure similar to that used in Example 1. The obtained cured resin plate was subjected to the measurement for the glass transition point Tg and the tensile modulus of elasticity E.

# EXAMPLE 5

[0096] A mixture of 90 parts by weight of EPICOAT 630 and 10 parts by weight of HELOXY 68 was employed as epoxy resins, and EPICURE W was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio R was set to 0.448.

[0097] Then a cured resin plate was prepared according to the procedure similar to that used in Example 1. The

obtained cured resin plate was subjected to the measurement for the glass transition point  $T_g$  and the tensile modulus of elasticity  $E$ .

#### EXAMPLE 6

[0098] A mixture of 90 parts by weight of EPICOAT 630 and 10 parts by weight of HELOXY 68 was employed as epoxy resins, and EPICURE W was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio  $R$  was set to 0.592.

[0099] Then a cured resin plate was prepared according to the procedure similar to that used in Example 2. The obtained cured resin plate was subjected to the measurement for the glass transition point  $T_g$  and the tensile modulus of elasticity  $E$ .

#### EXAMPLE 7

[0100] A mixture of 90 parts by weight of EPICOAT 630 and 10 parts by weight of HELOXY 68 was employed as epoxy resins, and ANCAMINE 2049 was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio  $R$  was set to 0.592.

[0101] Then a cured resin plate was prepared according to the following procedure;

- (1) raising the temperature of the composition at 1.5°C/min to 60°C,
- (2) maintaining the temperature at 60°C for 180 minutes,
- (3) raising the temperature at 1.5°C/min to 130°C,
- (4) maintaining the temperature at 130°C for 120 minutes, and
- (5) lowering the temperature at 2.5°C/min to 25°C.

[0102] The obtained cured resin plate was subjected to the measurement for the glass transition point  $T_g$  and the tensile modulus of elasticity  $E$ .

#### EXAMPLE 8

[0103] A mixture of 70 parts by weight of EPICOAT 630 and 30 parts by weight of EPOMIC R710 was employed as epoxy resins, and EPICURE W was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio  $R$  was set to 0.402.

[0104] Then a cured resin plate was prepared according to the procedure similar to that used in Example 1. The obtained cured resin plate was subjected to the measurement for the glass transition point  $T_g$  and the tensile modulus of elasticity  $E$ .

#### EXAMPLE 9

[0105] A mixture of 70 parts by weight of EPICOAT 630 and 30 parts by weight of GAN was employed as epoxy resins, and EPICURE W was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio  $R$  was set to 0.433.

[0106] Then a cured resin plate was prepared according to the procedure similar to that used in Example 1. The obtained cured resin plate was subjected to the measurement for the glass transition point  $T_g$  and the tensile modulus of elasticity  $E$ .

#### EXAMPLE 10

[0107] A mixture of 70 parts by weight of EPICOAT 630 and 30 parts by weight of GAN was employed as epoxy resins, and ANCAMINE 2049 was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio  $R$  was set to 0.572.

[0108] Then a cured resin plate was prepared according to the procedure similar to that used in Example 2. The obtained cured resin plate was subjected to the measurement for the glass transition point  $T_g$  and the tensile modulus

of elasticity E.

#### EXAMPLE 11

5 [0109] A mixture of 70 parts by weight of EPICOAT 630 and 30 parts by weight of DENACOL EX721 was employed as epoxy resins, and EPICURE W was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio R was set to 0.412.

10 [0110] Then a cured resin plate was prepared according to the procedure similar to that used in Example 1. The obtained cured resin plate was subjected to the measurement for the glass transition point Tg and the tensile modulus of elasticity E.

#### EXAMPLE 12

15 [0111] A mixture of 90 parts by weight of EPICOAT 828 and 10 parts by weight of HELOXY 68 was employed as epoxy resins, and isophorone diamine was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio R was set to 0.232.

20 [0112] Then a cured resin plate was prepared according to the procedure similar to that used in Example 7. The obtained cured resin plate was subjected to the measurement for the glass transition point Tg and the tensile modulus of elasticity E.

#### EXAMPLE 13

25 [0113] A mixture of 30 parts by weight of EPICOAT 630 and 70 parts by weight of EPICOAT 807 was employed as epoxy resins, and a mixture of 50 parts by weight of isophorone diamine and 50 parts by weight of ANCAMINE 2049 was employed as curing agents and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio R was set to 0.358.

30 [0114] Then a cured resin plate was prepared according to the procedure similar to that used in Example 7. The obtained cured resin plate was subjected to the measurement for the glass transition point Tg and the tensile modulus of elasticity E.

#### EXAMPLE 14

35 [0115] The same epoxy resin composition as that used in Example 5 was employed and a composite material was prepared according to the following procedure;

- (1) raising the temperature of the composition at 1.5°C/min to 60°C,
- (2) maintaining the temperature at 90°C for 600 minutes,
- 40 (3) raising the temperature at 1.5°C/min to 180°C,
- (4) maintaining the temperature at 180°C for 120 minutes, and
- (5) lowering the temperature at 2.5°C/min to 25°C.

45 [0116] The obtained composite material was observed with an optical microscope for the external surface and the cross section. No unimpregnated part or voids were observed and the quality of the product was good. The composite material was then subjected to the measurement for 0° compressive strength.

#### EXAMPLE 15

50 [0117] The same epoxy resin composition as that used in Example 6 was employed and a composite material was prepared according to the following procedure;

- (1) raising the temperature of the composition at 1.5°C/min to 60°C,
- (2) maintaining the temperature at 60°C for 180 minutes,
- 55 (3) raising the temperature at 1.5°C/min to 180°C,
- (4) maintaining the temperature at 180°C for 120 minutes, and
- (5) lowering the temperature at 2.5°C/min to 25°C.



[0118] The obtained composite material was observed with an optical microscope for the external surface and the cross section. No unimpregnated part or voids were observed and the quality of the product was good. The composite material was then subjected to the measurement for 0° compressive strength.

#### 5 COMPARATIVE EXAMPLE 1

[0119] EPICOAT 630 was employed as an epoxy resin, and JEFFAMINE D230 (registered trademark, manufactured by Jefferson Chemical Company, polyoxypropylene diamine, viscosity in 25°C environment: 9mPas,  $\beta=9.8$ ) was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio R was set to 0.621.

[0120] Then a cured resin plate was prepared according to the procedure similar to that used in Example 2. The obtained cured resin plate was subjected to the measurement for the glass transition point Tg and the tensile modulus of elasticity E.

#### 15 COMPARATIVE EXAMPLE 2

[0121] EPICOAT 828 was employed as an epoxy resin, and EPICURE W was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio R was set to 0.283.

[0122] Then a cured resin plate was prepared according to the procedure similar to that used in Example 1. The obtained cured resin plate was subjected to the measurement for the glass transition point Tg and the tensile modulus of elasticity E.

#### 25 COMPARATIVE EXAMPLE 3

[0123] EPICOAT 828 was employed as an epoxy resin, and ANCAMINE 2048 was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio R was set to 0.374.

[0124] Then a cured resin plate was prepared according to the procedure similar to that used in Example 2. The obtained cured resin plate was subjected to the measurement for the glass transition point Tg and the tensile modulus of elasticity E.

#### COMPARATIVE EXAMPLE 4

[0125] EPICOAT 828 was employed as an epoxy resin, and JEFFAMINE D230 was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio R was set to 0.379.

[0126] Then a cured resin plate was prepared according to the procedure similar to that used in Example 2. The obtained cured resin plate was subjected to the measurement for the glass transition point Tg and the tensile modulus of elasticity E.

#### COMPARATIVE EXAMPLE 5

[0127] A mixture of 40 parts by weight of EPICOAT 630 and 60 parts by weight of HELOXY 107 was employed as an epoxy resin, and EPICURE W was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio R was set to 0.354.

[0128] Then a cured resin plate was prepared according to the procedure similar to that used in Example 1. The obtained cured resin plate was subjected to the measurement for the glass transition point Tg and the tensile modulus of elasticity E.

#### COMPARATIVE EXAMPLE 6

[0129] A mixture of 70 parts by weight of EPICOAT 630 and 30 parts by weight of YED 216 (registered trademark, manufactured by Yuka Shell Epoxy K.K., 1,6-hexane diol diglycidyl ether, viscosity in 25°C environment: 15 - 35 mPas,  $\alpha=6$ ) was employed as epoxy resins, and EPICURE W was employed as a curing agent and the viscosity of each material and the viscosity of the resulting composition  $\eta_5$ ,  $\eta_{60}$ ,  $\eta_{120}$  and  $\eta_{240}$  after they were mixed were measured. Here, the mixing ratio R was set to 0.412.

[0130] Then a cured resin plate was prepared according to the procedure similar to that used in Example 1. The obtained cured resin plate was subjected to the measurement for the glass transition point T<sub>g</sub> and the tensile modulus of elasticity E.

#### COMPARATIVE EXAMPLE 7

[0131] The same epoxy resin composition as that used in Comparative Example 1 was employed and a composite material was prepared in a similar procedure as that used in Example 15.

[0132] The obtained composite material was observed with an optical microscope for the external surface and the cross section. No unimpregnated part or voids were observed and the quality of the product was good. The composite material was subjected to the measurement for 0° compressive strength.

#### COMPARATIVE EXAMPLE 8

[0133] The same epoxy resin composition as that used in Comparative Example 2 was employed and a composite material was prepared in a similar procedure as that used in Example 14.

[0134] At the end of the obtained composite material, there was a part which was not impregnated with the resin, and the quality of the product was poor.

TABLE 1

	Example 1	Example 2	Example 3	Example 4	Example 5
Epoxy resin compositions					
(Main Agent)					
EPICOAT 630 [3ArEp]	100	100	60	70	90
EPICOAT 807 [2ArEp]			40		
HELOXY 107 [2GIFaEp]				30	
HELOXY 68 [2GIFaEp]					10
(Curing Agent)					
EPICURE W [ArAm]	46.4		38.4	40.9	44.8
ANCAMINE 2049 [FaAm]		61.3			
Viscosity of Main Agent (mPa · s)	680	680	1180	278	362
Viscosity of Curing Agent (mPa · s)	187	120	187	187	187
Mixing Ratio R	0.464	0.613	0.384	0.409	0.448
η <sub>5</sub> (mPa · s)	670	270	980	344	474
η <sub>60</sub> (mPa · s)	675	292	988	346	477
η <sub>120</sub> (mPa · s)	678	332	995	351	480
η <sub>240</sub> (mPa · s)	690	420	1020	360	488
Curing Conditions					
T <sub>c</sub> (°C) highest temperature during the curing process	180	180	180	180	180
t <sub>c</sub> (min) retention time at the highest temperature	120	120	120	120	120
T <sub>c</sub> +20-kx(T <sub>c</sub> -90) (°C)	169	169	169	169	169
Physical properties of the cured resin					
Glass Transition Point T <sub>g</sub> (°C)	227	230	203	192	210
Tensile Modulus of Elasticity E (GPa)	3.6	3.6	3.3	3.5	3.5

TABLE 2

	Example 6	Example 7	Example 8	Example 9	Example 10
Epoxy resin compositions					
(Main Agent)					
EPICOAT 630 [3ArEp]	90	90	70	70	70
HELOXY 68 [2GIFaEp]	10	10			
EPOMIC R710 [2ArEp]			30		
GAN [2ArEp]				30	30
(Curing Agent)					
EPICURE W [ArAm]			40.2	43.3	
ANCAMINE 2049 [CyAm]	59.2	59.2			57.2
Viscosity of Main Agent (mPa · s)	362	362	1027	439	439
Viscosity of Curing Agent (mPa · s)	120	120	187	187	120
Mixing Ratio R	0.592	0.592	0.402	0.433	0.572
$\eta_5$ (mPa · s)	211	211	823	501	238
$\eta_{60}$ (mPa · s)	243	243	829	509	299
$\eta_{120}$ (mPa · s)	297	297	835	519	416
$\eta_{240}$ (mPa · s)	443	443	850	544	713
Curing Conditions					
Tc (°C) highest temperature during the curing process	180	130	180	180	180
tc (min) retention time at the highest temperature	120	120	120	120	120
Tc+20-kx(Tc-90) (°C)	169	136	169	169	169
Physical Properties of the Cured Resin					
Glass Transition Point Tg (°C)	222	171	211	205	211
Tensile Modulus of Elasticity E (GPa)	3.7	3.2	3.4	3.9	4.0

TABLE 3

	Example 11	Example 12	Example 13
Epoxy resin compositions			
(Main Agent)			
EPICOAT 630 [3ArEp]	70		30
DENACOL EX721 [2ArEp]	30		
EPICOAT 828 [2ArEp]		90	
EPICOAT 807 [2ArEp]			70
HELOXY 68 [2GIFaEp]		10	
(Curing Agent)			
EPICURE W [ArAm]	41.2		
ANCAMINE 2049 [CyArAm]			17.9
Isophorone Diamine [CyArAm]		23.2	17.9
Viscosity of Main Agent (mPa • s)	685	3600	1990
Viscosity of Curing Agent (mPa • s)	187	18	33
Mixing Ratio R	0.412	0.232	0.358
$\eta_5$ (mPa • s)	698	1020	465
$\eta_{60}$ (mPa • s)	709	2610	749
$\eta_{120}$ (mPa • s)	720	17400	1540
$\eta_{240}$ (mPa • s)	750	n/a	33600
Curing Conditions			
T <sub>c</sub> (°C) highest temperature during the curing process	180	130	130
t <sub>c</sub> (min) retention time at the highest temperature	120	120	120
T <sub>c</sub> +20-kx(T <sub>c</sub> -90) (°C)	169	136	136
Physical Properties of the Cured Resin			
Glass Transition Point T <sub>g</sub> (°C)	195	141	137
Tensile Modulus of Elasticity E (GPa)	3.9	3.3	3.4

TABLE 4

	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Epoxy resin compositions (Main Agent)						
EPICOAT 630 [3ArEp]	100	100	100	100	40	70
EPICOAT 828 [2ArEp]					60	30
HELOXY 107 [2GIPaEp]						
YED 216 [2GIPaEp]						
(Curing Agent)						
EPICURE W [ArAm]		28.3	37.4		35.4	41.2
ANCAFINE 2049 [CyAm]						
JEPFAMINE D230 [PaAm]	62.1			37.9		
Viscosity of Main Agent (mPa·s)	680	14600	14600	14600	138	52
Viscosity of Curing Agent (mPa·s)	9	187	120	9	187	187
Mixing Ratio R	0.621	0.283	0.374	0.379	0.354	0.412
$\eta_0$ (mPa·s)	73	5100	3410	513	202	209
$\eta_{60}$ (mPa·s)	84	5120	5240	1010	203	210
$\eta_{120}$ (mPa·s)	99	5160	9620	1840	203	212
$\eta_{180}$ (mPa·s)	139	5200	24200	4090	205	214
Curing Conditions						
Tc (°C) highest temperature during the curing process	180	180	180	180	180	180
tc (min) retention time at the highest temperature	120	120	120	120	120	120
Tc+20-kt(Tc-90) (°C)	169	169	136	169	169	169
Physical Properties of the Cured Resin						
Glass Transition Point Tg (°C)	151	197	203	129	128	167
Tensile Modulus of Elasticity E (GPa)	3.0	3.1	3.0	2.8	3.1	3.1

TABLE 5

	Example 14	Example 15	Comparative Example 7	Comparative Example 8
Epoxy Resin Compositions				
(Epoxy resin)				
EPICOAT 630 [3ArEp]	90	90	100	
HELOXY 68 [2GIFaEp]	10	10		
EPICOAT 828 [2GIFaEp]				100
(Curing Agent)				
EPICURE W [ArAm]	44.8			28.3
ANCAMINE 2049 [CyAm]		59.2		
JEFFAMINE D230 [FaArAm]			62.1	
Quality of the Product	Good	Good	Good	Inferior Impregnation
0°C Compressive Strength (MPa)	615	658	533	-

(Explanation of abbreviations used in Tables 1 - 5)

#### [0135]

[3ArEp]: tri-functional aromatic epoxy resin

[2ArEp]: di-functional aromatic epoxy resin

[2GeFaEp]: di-functional glycidyl ether type aliphatic epoxy resin

[ArAm]: aromatic amine compound

[CyAm]: alicyclic amine compound

[FaAm]: aliphatic amine compound

#### Industrial Applicability

[0136] According to the present invention, there is provided an epoxy resin composition having a low viscosity around the room temperature and excellent reinforcing fiber impregnating characteristics. By the use of such an epoxy resin composition, a composite material having excellent heat resistance and mechanical properties including a compressive strength can be produced.

[0137] The composite material obtained from the epoxy resin composition according to the present invention can be suitably applied for a structural component for an aircraft, artificial satellite, automobile, bicycle, railcar, ship, or building material, flywheel, oil riser and sporting-goods and the like. It can be particularly preferably employed for a structural component for an aircraft and artificial satellite which require high heat resistance.

#### Claims

1. An epoxy resin composition comprising an aromatic epoxy resin having at least di-functionality, an aromatic amine compound and/or an alicyclic amine compound, wherein 5 minutes after the main agent comprising the epoxy resin and the curing agent comprising the aromatic amine compound and/or the alicyclic amine compound are mixed at 25°C, the composition shows a viscosity at 25 °C in a range of from 1 to 1500 mPas, and Tc, tc, and Tg satisfy the following equation.

$$T_g \geq T_c + 20 - k \times (T_c - 90) \quad (1)$$

k = 0 when  $60 \leq T_c < 90$

k = 0.35 when  $90 \leq T_c \leq 200$

Tc: highest temperature (°C) during the curing process ( $60 \leq T_c \leq 200$ )

tc: retention time (min) at the highest temperature ( $1 \leq t_c \leq 120$ )

Tg: glass transition temperature of the epoxy resin composition after a lapse of  $t_c$  (min) at  $T_c$  (°C).

2. An epoxy resin composition according to claim 1 in which the aromatic epoxy resin having at least tri-functionality.
3. An epoxy resin composition according to claim 2, in which the amount of the aromatic epoxy resin having at least tri-functionality blended is 50 - 100 % by weight of the total amount of the epoxy resin.
4. An epoxy resin composition according to claim 2, or claim 3, wherein the viscosity of the aromatic epoxy resin having at least tri-functionality at 25°C is within the range of from 1 to 3,000 Pas.
5. An epoxy resin composition according to any one of claim 1 - claim 4, wherein the viscosity of the epoxy resin composition 5 minutes after the mixing at 25°C is within the range of from 1 to 1,000 mPas.
6. An epoxy resin composition according to any one of claim 1 - claim 5, wherein the tensile modulus of elasticity of the cured resin product produced from the epoxy resin composition is within the range of from 3.2 to 5 GPa at 23°C.
7. An epoxy resin composition according to any one of claim 1 - claim 6, which satisfies the following equations (2) and (3).

$$1 \leq \eta_{60} \leq 1500 \quad (2)$$

$$1 \leq \eta_{60}/\eta_5 \leq 3 \quad (3)$$

$\eta_5$ : the viscosity (mPas) of the epoxy resin composition at 25°C after the main agent and the curing agent are mixed and allowed to stand for 5 minutes at 25°C.

$\eta_{60}$ : the viscosity (mPas) of the epoxy resin composition at 25°C after the main agent and the curing agent are mixed and allowed to stand for 60 minutes at 25°C.

8. An epoxy resin composition according to any one of claim 1 - claim 6, which satisfies the following equations (2') and (3').

$$1 \leq \eta_{240} \leq 1000 \quad (2')$$

$$1 \leq \eta_{240}/\eta_5 \leq 3 \quad (3')$$

$\eta_5$ : the viscosity (mPas) of the epoxy resin composition at 25°C after the main agent and the curing agent are mixed and allowed to stand for 5 minutes at 25°C.

$\eta_{240}$ : the viscosity (mPas) of the epoxy resin composition at 25°C after the main agent and the curing agent are mixed and allowed to stand for 240 minutes at 25°C.

9. An epoxy resin composition according to any one of claim 1 - claim 8, which further comprises a glycidyl ether type aliphatic epoxy resin having at least di-functionality.
10. An epoxy resin composition according to claim 9, in which the glycidyl ether type aliphatic epoxy resin having at least di-functionality satisfies the following equation (4).

$$0 \leq \alpha \leq 4 \quad (4)$$

$\alpha$ : a number of (carbon) atoms which do not belong to a ring in the molecular chain which is produced by linking any two glycidyl oxy groups in a glycidyl ether type aliphatic epoxy resin having at least di-functionality, provided that the molecular chain has the largest number of (carbon) atoms which do not belong to a ring.

11. An epoxy resin composition according to claim 9 or claim 10, in which the glycidyl ether type aliphatic epoxy resin having at least di-functionality is blended in an amount of 1 - 50 % by weight based on the total amount of the epoxy resin.

12. An epoxy resin composition according to any one of claim 1 - claim 11, which comprises an aromatic amine compound and the viscosity of the aromatic amine compound at 25°C is within the range of from 1 to 3000 mPas.

13. An epoxy resin composition according to any one of claim 1 - claim 12, which comprises an alicyclic amine compound and the viscosity of the alicyclic amine compound at 25°C is within the range of from 1 to 500 mPas.

14. An epoxy resin composition according to any one of claim 1 - claim 13, which comprises an alicyclic amine compound and the alicyclic amine compound satisfies the following equation (5).

$$0 \leq \beta \leq 4 \quad (5)$$

$\beta$ : a number of (carbon) atoms which do not belong to a ring in the molecular chain which is produced by linking any two amino groups in an alicyclic amine compound, provided that the molecular chain has the largest number of (carbon) atoms which do not belong to a ring.

15. An epoxy resin composition according to any one of claim 1 - claim 14, which comprises an alicyclic amine compound and the alicyclic amine compound contains an amino group bonded to secondary or tertiary carbon atom in the molecule.

16. An epoxy resin composition according to claim 15, in which all the amino groups in the molecule of the alicyclic amine compound are bonded to secondary or tertiary carbon atoms.

17. An epoxy resin composition for a fiber reinforced composite material, which comprises an epoxy resin composition according to any one of claim 1 - claim 16.

18. A fiber reinforced composite material comprising a cured product of an epoxy resin composition according to any one of claim 1 - claim 17, and a reinforcing fiber.

19. A fiber reinforced composite material according to claim 17, in which the reinforcing fiber is carbon fiber.



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/01462

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.<sup>7</sup> C08G59/50, C08L63/00, C08K7/02, C08J5/24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.<sup>7</sup> C08G59/50, C08L63/00-10, C08K7/02-14,  
C08J5/24

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
WPI/L

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, 559607, A2 (CIBA-GEIGY AKTIENGESELLSCHAFT), 08 September, 1993 (08.09.93), Claims & JP, 6-41397, A, Claims	1-19
A	EP, 604909, A2 (HERCULES INCORPORATED), 06 July, 1994 (06.07.94), Claims & JP, 7-2974, A, Claims & US, 5360846, A	1-19
A	JP, 9-25393, A (Toray Industries, Inc.), 28 January, 1997 (28.01.97), Claims & EP, 742266, A2	1-19
A	JP, 5-320480, A (Toray Industries, Inc.), 03 December, 1993 (03.12.93), Claims (Family: none)	1-19
A	JP, 8-225666, A (Toray Industries, Inc.), 03 September, 1996 (03.09.96), Claims (Family: none)	1-19

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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06 June, 2000 (06.06.00)Date of mailing of the international search report  
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